LA-UR-03-7320

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Title: Demonstration of a Multi-Layered Permeable Reactive Barrier in Mortandad Canyon at Los Alamos National Laboratory

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Submitted to: US DOE Environmental Management

Los Alamos NATIONAL LABORATORY

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Work Proposal Number: AL11SS31

FAO (DOE/AL) Field Office

B&R Code: EW40CT010

LAUR #03-7320

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1.0 Executive Summary

A multi-layered permeable reactive barrier (PRB) has been installed in Mortandad Canyon, on the Pajarito Plateau in the north-central part of LANL, to demonstrate *in-situ* treatment of a suite of contaminants with dissimilar geochemical properties. The PRB will also mitigate possible vulnerabilities from downgradient contaminant movement within alluvial and deeper perched groundwater. Mortandad Canyon was selected as the location for this demonstration project because the flow of alluvial groundwater is constrained by the geology of the canyon, a large network of monitoring wells already were installed along the canyon reach, and the hydrochemistry and contaminant history of the canyon is well-documented.

The PRB uses a funnel-and-gate system with a series of four reactive media cells to immobilize or destroy contaminants present in alluvial groundwater, including strontium-90, plutonium-238, 239, 240, americium-241, perchlorate, and nitrate. The four cells, ordered by sequence of contact with the groundwater, consist of gravel-sized scoria (for colloid removal); phosphate rock containing apatite (for metals and radionuclides); pecan shells and cotton seed admixed with gravel (bio-barrier, to deplete dissolved oxygen and destroy potential RCRA organic compounds, nitrate and perchlorate); and limestone (pH buffering and anion adsorption). Design elements of the PRB are based on laboratory-scale treatability studies and on a field investigation of hydrologic, geochemical, and geotechnical parameters. The PRB was designed with the following criteria:
1-day residence time within the bio-barrier, 10-year lifetime for the PRB, minimization of surface water infiltration and erosion, optimization of hydraulic capture, and minimization of excavated material requiring disposal. Each layer has been equipped with monitoring wells or ports to allow sampling of groundwater and reactive media, and monitor wells are located immediately adjacent to the up- and down-gradient perimeter of the engineered structure.

Groundwater sampling upgradient, within, and downgradient of the PRB took place from May through August 2003. Concentrations of strontium-90 have diminished by 80% and 40% within the central portion of the phosphate rock (apatite) and bio-barrier cells, respectively. Higher concentrations of this radionuclide occur in groundwater near the north and south perimeters of the two cells. The non-uniform distribution of strontium-90 may result from varying residence time and saturated thickness of pore water. Initial concentrations of nitrate (8-12 parts per million or ppm as nitrate) and perchlorate (0.035 ppm) have been reduced in the phosphate rock and bio-barrier cells to concentrations that are less than method detection limits (0.01 and 0.002 ppm, respectively). Initial microbial analyses suggest the presence of both dissimilatory perchlorate- and nitrate-reducing bacterial populations, along with production of acetate and propionate, and decreasing dissolved oxygen and pH. The dominant group of perchlorate reducers consists of members of the previously described *Dechloromonas* genus, in the beta subclass of the Proteobacteria, which together with the *Dechlorosoma* genus are considered to be the dominant genera in circum-neutral mesophilic environments.

Groundwater flow through the multiple PRB is taking place at a very slow rate based on similar concentrations of nitrate, perchlorate, chlorate, and chlorite in the upgradient well MCO-4B and downgradient well MCO-5. Concentrations of these constituents also increase within the limestone cell. Decreased precipitation due to extreme drought is probably responsible for decreasing saturated thickness within both the alluvium and PRB, resulting in stagnant conditions. Varying distributions of ammonium, nitrate, sulfate, iron, and manganese within the phosphate rock, bio-barrier, and limestone cells also support this hypothesis.

2.0 Introduction

In January and February 2003, Los Alamos National Laboratory (LANL) installed a multi-layered permeable reactive barrier (PRB) in Mortandad Canyon to demonstrate *in-situ* treatment of a suite of contaminants in shallow alluvial groundwater and to mitigate possible vulnerabilities from downgradient contaminant migration within alluvial and deeper perched groundwater. The contaminant suite, consisting of isotopic strontium, plutonium, and americium, perchlorate, and nitrate, displays a wide range of geochemical properties and is not amendable to standard treatment approaches. The sequential layering of reactive media to promote agglomeration of radionuclide-bearing colloids, chemical fixation of metals and radionuclides, and biodegradation of nitrate and perchlorate is a novel approach to resolving the problem of multi-variant contaminant suites. Given the prevalence of multiple contaminant suites at facilities within the U.S. Department of Energy (DOE) complex, and the growing issue of perchlorate in groundwater, the PRB installed in Mortandad Canyon represents an important technology enhancement to the complex.

This document presents background information for the project, describes the design, and evaluates performance of the PRB. Additional information, including detailed design drawings, photographs depicting the installation process, details of the geochemistry and biochemistry of the reactive cells, and miscellaneous data are included as appendices.

3.0 Background

Mortandad Canyon, located on the Pajarito Plateau in the north-central part of LANL (Figure 3.0-1), was selected as the location for the PRB for the reasons listed below.

1) The LANL Radioactive Liquid Waste Plant at Technical Area 50 (Figure 3.1) has discharged treated waste effluents into Mortandad Canyon since 1963 (Purtymun et al., 1983). The amount and quality of these discharges, and their impact to alluvial and perched intermediate-depth groundwater in Mortandad Canyon, are well documented (Broxton et al., 2002; Purtymun et al., 1977; Purtymun et al., 1983; Marty et al., 1997).
2) Initial fieldwork for this project (Shaw Corporation, 2001) verified that the flow of alluvial groundwater is constrained by the geology of the canyon. Reactive barriers installed at other DOE sites have failed to perform as expected because of poor hydraulic control of the system.
3) A large network of monitoring wells have already been installed along the canyon reach (Appendix E), providing opportunity for performance evaluation at a range of length scales.
4) A number of reports and data sets have been published on the geochemistry of the alluvial groundwater (Purtymun et al., 1983; Purtymun, 1995; LANL, 2002), thus documenting the hydrochemistry of the canyon.

Historic discharges from the Radioactive Liquid Waste Plant have introduced radionuclides, nitrogen species (nitrate and total Kjeldahl nitrogen) and perchlorate into

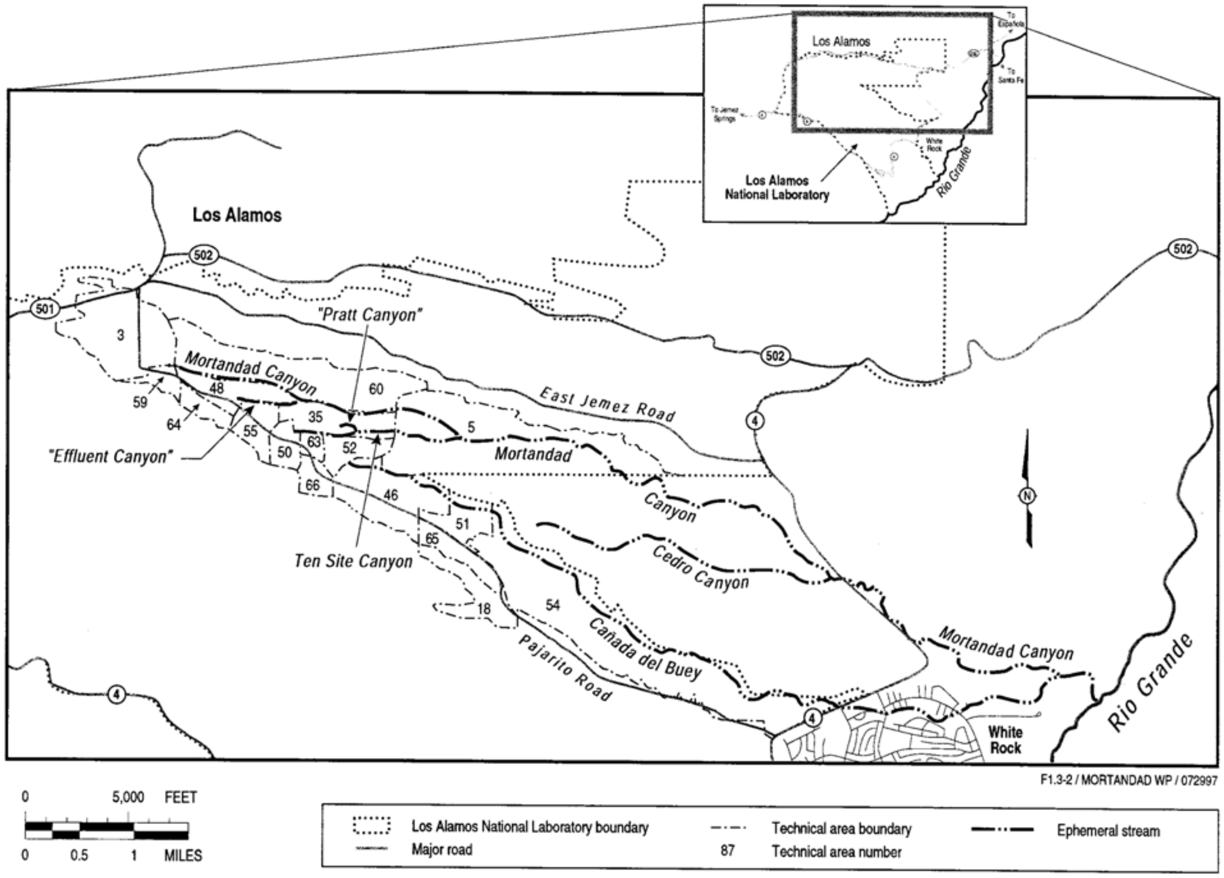

Figure 3.0-1. Location of Mortandad Canyon within Los Alamos National Laboratory.

the alluvial groundwater. The radionuclides, americium-241, cesium-137, plutonium-238, 239, 240, and strontium-90, occur as dissolved aqueous species and as colloids possibly composed of calcium carbonate, silica, ferric(oxy)hydroxide, and solid organic matter. Plutonium and nitrate occur in concentrations below groundwater action levels, whereas strontium-90, americium-241, and perchlorate exceed action levels (Table 3-1).

Table 3-1. Summary of Groundwater Data for Mortandad Canyon

Constituent	Concentration	Action Level	Comment
^{90}Sr	80 pCi/L	8 pCi/L	DCG
^{238}Pu	1.182 pCi/L	1.6 pCi/L	DCG
$^{239,240}Pu$	0.61 pCi/L	1.2 pCi/L	DCG
^{241}Am	1.53 pCi/L	1.2 pCi/L	DCG
Nitrate (N)	5.7 mg/L	10 mg/L	MCL
Perchlorate	120-250 ppb	4 μg/L	Proposed EPA MCL

Data from monitoring well MCO-4B upgradient from the multiple PRB (LANL, 2002). DCG is derived concentration guideline from DOE. MCL = maximum contaminant level.

LANL conducted laboratory-scale treatability studies with a suite of reactive barrier materials to quantitatively evaluate the performance of these materials in Mortandad Canyon groundwater, to guide the selection of materials for the PRB, and to develop design criteria for full-scale installation of the PRB. LANL retained Shaw Environmental, Inc. (Shaw) as a contractor with design and installation experience in reactive barrier technology to perform a number of tasks. Under LANL direction, Shaw conducted geotechnical and hydrogeologic investigations (Shaw Corporation, 2001) to determine contaminant concentrations and distributions within soil and groundwater, alluvial aquifer thickness and lateral extent, bedrock and groundwater elevations, hydraulic conductivity of the alluvium and underlying bedrock, grain size distribution of the soils, and soil moisture. These data verified that bedrock underlying the alluvium would provide a lower boundary for the PRB sufficient for hydraulic containment, construction of a PRB would be geotechnically feasible, and excavated soils could be economically disposed as low-level radioactive waste. Based on these data, LANL directed Shaw to 1) prepare conceptual and final detailed engineered designs (Shaw Environmental, 2001, 2002) that included hydraulic and geochemical modeling of the system and 2) install the PRB.

4.0 PRB Design and Construction

Design elements of the PRB are based on data gathered in laboratory-scale treatability studies (Conca et al., 2002) and in the initial field investigation (Shaw Corporation, 2001) as well as influent chemistry (Table 3-1) and treatment goals. The PRB was designed with the following criteria:

1) Treatment of a diverse contaminant suite comprised of radionuclides (americium-241, plutonium-238, 239, 240, and strontium-90), nitrate, and perchlorate,
2) One-day residence time within the biobarrier,
3) Ten-year lifetime for the PRB,
4) Minimization of surface water infiltration and erosion,
5) Optimization of hydraulic capture,
6) Minimization of excavated material requiring disposal,
7) Installation of ports in each cell to allow sampling of water and reactive media, and
8) Installation of monitor wells immediately adjacent to the up- and down-gradient perimeters of the PRB.

The PRB consists of four sequential reactive media cells (Figure 4.0-1). The first cell contains porous volcanic rock (scoria) gravel for colloid removal. The second cell contains phosphate rock containing mineral apatite (calcium phosphate) for removal of metals and radionuclides by adsorptive processes and mineral co-precipitation. The third cell is a bio-barrier, consisting of 10% cottonseed meal, 65% pecan shells, and 25% pea gravel (by volume), to enhance anaerobic conditions by depleting dissolved oxygen and transforming nitrate and perchlorate through biochemical degradation. The fourth cell contains limestone gravel as a final pH control and polishing agent by adsorbing anionic complexes of plutonium(IV) and americium(III).

Given these diverse reaction processes, residence time, kinetics, and contaminant retardation factors were considered in the design. In addition, Darcy's Law parameters, including hydraulic conductivity, hydraulic gradient, and cross-sectional area, were also considered. The resulting numerical flow modeling provided a means to estimate groundwater flow under heterogeneous conditions in which flow parameters vary considerably, both for pre-installation conditions and in the presence of the PRB. Evaluation of residence time and groundwater flow determined the quantity of reactive media required to achieve treatment goals.

The following sections summarize the various design components of the PRB, including hydraulic, geochemical, and geotechnical parameters. Details of the voluminous supporting calculations are presented in the final design report (Shaw Environmental, 2002). Detailed design drawings are presented in Appendix A. Photo documentation of the installation and other field activities is presented in Appendix B.

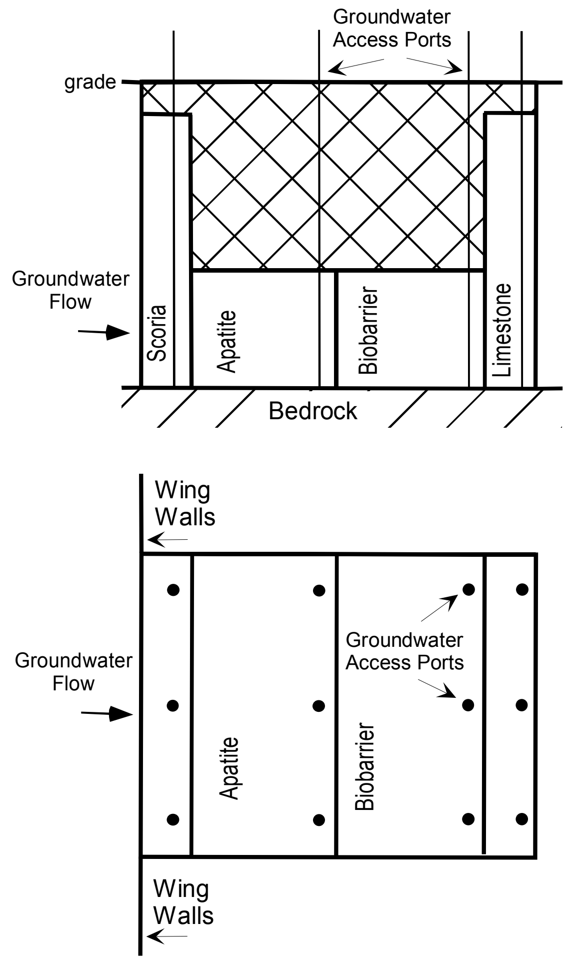

Figure 4.0-1. Schematic diagram depicting design of PRB in cross-sectional (top) and plan (bottom) views (not to scale). Total depth of PRB is 27 feet. The gate contains the four sequential media cells consisting of scoria gravel (3.7 feet thick), apatite gravel (8 feet), pecan shells/cottonseed with an admixture of gravel (biobarrier, 9.7 feet), and limestone gravel (3.7 feet). The funnel (wing walls) directs the alluvial groundwater through the gate. Sampling ports consist of 2-inch PVC with 10 feet of screen. Monitor wells (not shown) are located at up- and down-gradient positions. Groundwater flows east to west in both figures.

4.1 Hydraulic Design

A numerical model of groundwater flow was constructed to simulate hydrogeologic conditions in Mortandad Canyon. The computer program MODFLOW (McDonald and Harbaugh, 1988), a three-dimensional finite-difference groundwater flow model, was used for the simulations. The model was calibrated to the natural groundwater flow conditions in Mortandad Canyon during June 2001, and then used to simulate flow with the PRB (funnel-and-gate) in place. The model was used to estimate two conditions of flow through the PRB. A flow rate of 163 ft^3/day (4.6 m^3/day) was estimated for the average flow (calibrated) condition and a rate of 500 ft^3/day (14.2 m^3/day) was estimated for a high flow condition. The dimensions of the multi-barrier gate were determined considering the residence time of groundwater within each cell. The fluctuating nature of the groundwater table was also considered for average and high flow conditions. The first and last cells (volcanic gravel and limestone) were extended over much of the thickness of the alluvial sequence, including the upper portion that is only periodically saturated to promote flow into and from the gate. The second and third cells (phosphate rock and bio-barrier) extend only through the lower portion of the alluvium, *i.e.*, the portion that remains saturated most of the year during average flow conditions. This design avoids periodic wetting and drying of the middle cells and also configures the cells so that the reactive material is used efficiently by remaining saturated, except perhaps during potential drought cycles. The velocities of groundwater movement and the residence times within the cells were calculated based on cell dimensions, flow rate, and porosity (Table 4.1-1).

Table 4.1-1. Hydraulic Properties of PRB Cells

Reactive Media	Dimensions[1] (feet)	Volume ($feet^3$)	Porosity[2]	Average Velocity (feet/day)	Average Residence Time (days)	High-Flow Velocity (feet/day)	High-Flow Residence Time (days)
Volcanic Gravel	Y = 3.5 Z = 20	1190	0.5	1.9	1.8	2.9	1.2
Mineral Apatite	Y = 7 Z = 10	1190	0.5	1.9	3.6	5.9	1.2
Pecan Shells and Cottonseed Meal (biobarrier)	Y = 9 Z = 10	1530	0.45	2.1	4.2	6.5	1.4
Limestone Gravel	Y = 3.5 Z = 20	1190	0.5	1.9	1.8	2.9	1.2

[1]X is the dimension perpendicular to flow, and is 17 ft for all cells. Y is the dimension parallel to flow. Z is cell height. Cells with Z = 10 ft are capped with low permeability soils and a geosynthetic clay liner to direct groundwater flow through the reactive medium.
[2]Total porosity of the bio-barrier is approximately 0.5, but due to possible generation of gas, an effective porosity of 0.45 is assumed for the bio-barrier.

The estimated residence times exceeded the design criterion for average and high flow conditions for each of the four reactive cells. The minimum residence time under the average flow condition is 1.8 days in the volcanic gravel and limestone gravel cells. Residence times in the phosphate rock and bio-barrier cells are 3.6 and 4.2 days, respectively. Under the high groundwater-flow condition, the minimum residence time is 1.2 days in the volcanic gravel, phosphate rock, and limestone gravel cells, and residence time in the bio-barrier is 1.4 days.

4.2 Geochemical Design

Estimated breakthrough times for the three radionuclides of interest, americium-241, plutonium-238, 239, 240, and strontium-90, were calculated for the phosphate rock cell based on hydraulic properties (Table 4.1-1) and the batch adsorption data determined in laboratory treatability studies (Conca et al., 2002). The estimated breakthrough times for americium-241, plutonium-238, 239, 240, and strontium-90 are 2.3, 42.0, and 57.2 years, respectively. The radionuclide with the lowest distribution coefficient and shortest breakthrough time is strontium-90. Removal of strontium-90 from groundwater, however, should be accomplished by adsorption processes occurring both the phosphate rock and bio-barrier cells. In the cell consisting of phosphate rock, the estimated breakthrough times for amercium-241 and plutonium-238,239,240 exceed the 10-year design criteria.

The geochemistry of the PRB was modeled to evaluate mineral equilibrium and the potential for precipitation of secondary phases, which could provide additional adsorptive sites and potentially decrease the effective porosity within the engineered structure. Computer simulations of the sequential chemical interactions that will occur as groundwater passes through each of the four cells of the PRB were simulated using the EQ3/6 geochemical modeling software package (Wolery, 1992). Simulations of the multi-cell PRB were performed by using the predicted pore water composition from the previous cell as input to the next cell. Results of these simulations provided the changes in solution composition, pH, and redox as a function of the mass of reactants added, and also provided the mass of original reactants consumed and the mass of new minerals precipitated in each of the sequential PRB cells.

Plutonium concentrations measured in the canyon water are oversaturated with respect to several plutonium(IV) minerals. These concentrations are most likely dominated by plutonium pseudocolloids, which are targeted for removal by the colloid barrier. Concentrations of plutonium that exit the colloid barrier should be further lowered by the bio-barrier, which maintains reducing conditions under which plutonium mobility is quite low. The PRB effluent is predicted to have a plutonium concentration of 3.65E-11 mg/L. Uranium is predicted to behave similar to plutonium, in that the suspended fraction will be removed by the colloid barrier, and the bio-barrier will remove some fraction of the remaining dissolved uranium via precipitation in a reducing environment. The PRB effluent is predicted to have a uranium concentration of 0.0001 mg/L. No effects on the concentrations of americium or strontium are predicted by the model, because these elements are undersaturated in all of the pore water compositions. However, strontium and americium concentrations will most likely be lowered by adsorption within the two cells consisting of phosphate rock and bio-barrier, but the model was not able to simulate those reactions.

Predicted decreases in uranium in groundwater exiting the PRB were greater than one order of magnitude, and decreases in plutonium were greater than three orders of magnitude. Perchlorate was predicted to be completely removed within the bio-barrier cell by microbially-mediated reduction to chloride. In a similar manner, nitrate was predicted to be completely converted within this cell by microbially-mediated reduction to a mixture of ammonia and nitrogen gas (N_2). The yield of ammonia versus nitrogen gas reaction products is controlled by the particular microbial pathways. These reactions cannot be accurately predicted with EQ3/6. However, an upper bound on nitrogen gas production could be based on the complete conversion of nitrate in the influent (4.4 mg/L as nitrogen) to nitrogen gas in the effluent. In addition to the modeling results, substantial removal of americium-241 and strontium-90 were predicted due to strong adsorption onto colloids potentially being removed by the colloid barrier. Adsorption of soluble plutonium, americium, and metals in both cells containing phosphate rock and bio-barrier should also take place.

No precipitation of any new phases was predicted for the PRB, with the minor exception of very small amounts of uraninite (UO_2) within the bio-barrier. If the addition of carbon dioxide and methane were allowed to continue within the bio barrier cell, then sulfate would reduce to sulfide. Under these conditions, iron as well as the trace metals nickel, lead, copper, and zinc, may precipitate as sulfide minerals, which have very low solubilites under sulfate-reducing conditions. These sulfide minerals would occupy some small fraction of the porosity within the bio barrier cell. It is doubtful, however, that this effect would have any significant effects on permeability for several reasons:

1) residence time within the bio-barrier cell is most likely too short to establish sulfate-reducing conditions,
2) the concentrations of metals that are prone to precipitation as sulfides are low, and
3) the pecan shell and cotton seed meal matrix of the bio-barrier cell will maintain a high porosity that can tolerate a significant amount of precipitation before the permeability is negatively affected.

In addition, the organic material within the bio-barrier cell will slowly convert to carbon dioxide and methane through microbial processes. The increase in porosity from the consumption of reactive organic compounds would most likely compensate for any loss in porosity by mineral precipitation. For these reasons, no loss in porosity from mineral precipitation is predicted within the PRB. This finding is significant, as failure in reactive barriers at other sites is often due to pore plugging from mineral precipitation.

4.3 Civil Engineering Design

The PRB consists of a funnel and gate constructed of sealable sheet piling driven through the alluvium layer and founded into the underlying bedrock. The gate is a braced cofferdam containing the four sequential media cells. The funnel directs the alluvial groundwater through the gate. The following subsections present a description of the funnel and gate system and the various civil engineering components and geotechnical parameters used in the PRB.

4.3.1 Gate Design

During the geotechnical investigation (Shaw Corporation, 2001), Standard Penetration Tests (SPT) and slug tests were conducted in the alluvium along the proposed PRB location. Based on the results of these tests and subsequent grain size distribution tests, the gate was located within the deepest portion of the asymmetric bedrock trough (Appendix A). At this location, SPT results yielded average blowcounts of 10 over a 2-foot (0.61 meter) interval, resulting in an average N-value of 5 blows per foot. Using the correlation between N-values and geotechnical properties (Bowles, 1982), the following geotechnical parameters were selected and used as the basis for the design:

1) γ (unit weight) = 110 pounds per cubic feet (lb/ft^3) (1.76 grams per cubic cm [g/cm^3]),
2) γ_{sat} (saturated unit weight) = 115 lb/ft^3 (1.84 g/cm^3),
3) q_u (unconfined compressive strength) = 0 pounds per square feet (lb/ft^2),
4) c (cohesion) = 0 lb/ft^2, and
5) ϕ (friction angle) = 28 degrees.

The gate is designed as a braced cofferdam, which consists of sheet piling, driven through the alluvium layer and founded into the underlying bedrock. The sheet piling was braced using three rows of walers. A soil pressure diagram/distribution developed by Peck and Terzaghi (Bowles, 1982) was used in the analyses. The design also considered the surcharge loading from a Caterpillar 300B excavator. This surcharge load was modeled to determine the additional lateral soil pressure diagram/distribution, using Boussinesq's stress influence charts for a strip loading. The system was also modeled using the SPW911 Version 2 computer model (PileBuck, 2001) to verify the design. This computer model yielded results similar to that of the manual calculations.

To provide separation between individual media layers, dividers constructed of type V steel mesh with 11/16-inch openings were installed. Media was placed within the cells in small increments of 1 to 2-foot (0.30 to 0.61 meter) and brought up simultaneously with less than 2-foot (0.61 meter) differential height between them. The media and backfill were not compacted to maximize permeability within the gate. A geotextile filter fabric was placed behind the grating of the first cell and in front of the grating of the fourth cell, to ensure soil backfill does not mix with reactive media. To prevent infiltration and erosion, a cover system has been provided over the gate. This cover consists of a geosynthetic clay liner (GCL) overlain by a protective soil cover and protective gravel layer. The surface of the cover system is also sloped to promote drainage.

4.3.2 Sampling Ports and Monitor Wells

A series of sampling ports and monitoring wells were installed upgradient, downgradient, and within the multiple PRB. Sampling ports and monitoring wells consisted of 2-inch (5.08 cm) polyvinyl chloride (PVC) pipe. Three groundwater-sampling ports are provided within each media layer to monitor PRB performance within each individual treatment cell and to obtain media specific data. The sampling wells are spaced 4 feet (1.2 meters) apart and are located in the downgradient portion of each media cell. These wells were installed during construction of the gate and are anchored to the media divider system. Each port is screened 10 feet (3.05 meters) above the base of the gate. Monitoring wells MCO-4B (upgradient to the PRB) and MCO-5 (downgradient to the PRB) previously installed by LANL in the early 1960s were also sampled as part of the performance assessment for the multiple PRB.

Fourteen sampling ports were installed within the PRB cell to provide the capability to sample the solid media. The ports consist of 2-inch (5.08 cm) PVC pipes installed through the holes within the walers and capped at the surface. Four ports provide access to the phosphate rock cell and six ports provide access to the bio-barrier cell. Two ports each provide access to both the volcanic gravel and the limestone cells.

One upgradient well and three downgradient wells were installed (Appendix E), continuously screened within the alluvium. The upgradient well was placed 6 feet (1.52 meters) upstream (west) of the PRB gate, aligned with the midpoint of the gate. The downgradient wells are located at 6, 51, and 100 feet (1.52, 10.5, 30.5 meters) downstream (east) of the midpoint of the gate. These wells will provide the capability to monitor groundwater flow and chemistry throughout the alluvium, which is necessary to assess PRB performance over time.

4.3.3   Funnel Design

The funnel directs alluvial groundwater so that the majority of it will flow through the gate. This funnel consists of a row of sheet piles driven through the alluvium and into the underlying bedrock. The joints of the funnel sheet piling are sealed to optimize flow through the gate and to create an impermeable barrier. The joint is coated with A-50 waterstop to reduce the potential for leakage through the funnel. In addition, the funnel is structurally tied into the up-gradient corners of the gate.

The north end of the funnel is keyed into the bedrock sidewall to prevent bypass around the wall. A trench was excavated along the canyon wall to bedrock. The trench was backfilled with bentonite to the elevation corresponding to the height of the gate and backfilled to the surface with previously excavated soils. Sheet piling was installed through the trench.

4.3.4   Construction

Construction of the PRB (Appendix B) including stream channel diversion, installation of the sealable sheet piling, excavation, construction de-watering, media placement, monitoring port installation, waste management, and site restoration including rip-rap placement and re-seeding for erosion control. Installation began in early January 2003 and was completed in the last week of February 2003. Due diligence testing was performed on reactive materials delivered to the project site before these materials were installed in the PRB. Results of due diligence testing is presented in Appendix E.

The monitor wells were installed in late July 2003. This delay in activity was needed to accommodate ecological restrictions associated with spotted owl nesting (March through May) and fire restrictions associated with the drought (June and July).

The bottom center of the PRB was over-excavated due to the construction methods employed. At the time of installation, the over-excavated depth was estimated to be approximately 3.3 feet (Appendix A, Sheet C3, Section A). PRB performance will not be impacted by this over excavation as the extra depth was backfilled with reactive media. Estimation of the over-excavated depth was later revised to approximately 4.5 feet based on subsequent well drilling and sounding of ports within the PRB.

Surface settlement has taken place over the PRB since installation was completed. Settlement was expected and its effects taken into account during the design phase. Consequently, the overall performance of the PRB will not be impacted by this phenomena (refer to Shaw E&I letter report, Appendix E).

5.0 PRB Performance

This section provides a discussion on water level measurements and alluvial groundwater hydrology, groundwater sampling, analytical methods, and evaluation of contaminant distributions within the PRB. Additional geochemical and biochemical information and detailed analytical results are provided in Appendices C and D, respectively. Perchlorate and strontium-90 were considered to be the most important contaminants in alluvial groundwater because they exceed an established MCL (8 pCi/L for strontium-90) and a proposed groundwater risk level (0.004 mg/L for perchlorate). Other contaminants, including isotopic plutonium, nitrate, fluoride, and total dissolved solids (TDS), are of secondary importance because they are present in treated Laboratory effluent and their concentrations in alluvial groundwater are currently below regulatory limits.

Groundwater samples were collected and analyzed from May through August 2003. Three sampling rounds were conducted during this time period. Monitoring wells sampled as part of this investigation included MCO-4B and MCO-5 and eight sampling ports within the multiple PRB. These included ports installed within the gravel cell (center port, Figure 4.0-1), phosphate rock cell (all three ports), bio-barrier cell (all three ports), and the limestone cell (center port). Three of the four monitoring wells installed in July (the upgradient well and two downgradient wells located at 6 and 51 feet from the PRB) were sampled during the third sampling round conducted in August 2003. The fourth well, MW-4 was dry and no samples were collected. Field parameters and water level measurements were taken from all wells and ports during the three sampling rounds.

5.1 Geohydrology

An evaluation of the hydrogeology within Mortandad Canyon for spring and summer 2003 is depicted in Figure 5.1-1. Between mid-May and mid-September, 2003, the saturated thickness of alluvium in the vicinity of the PRB has decreased. The initial thickness of approximately 2.5 feet diminished to less than one foot by August. Downgradient monitor wells installed at the PRB became dry in August, and the

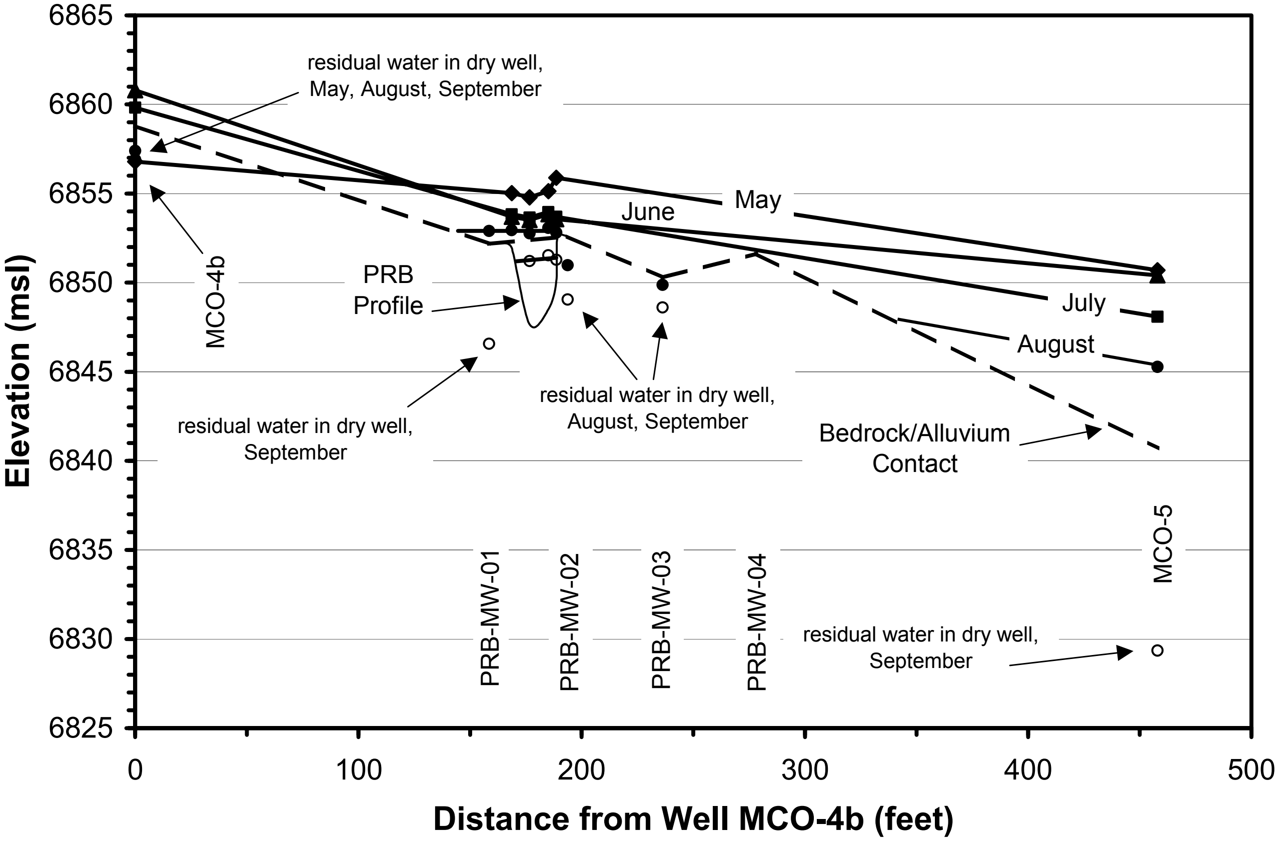

Figure 5.1-1 Hydrogeologic cross-section from west to east through monitor well MCO-4B, the PRB, and monitor well MCO-5 in Mortandad Canyon. Locations of the PRB monitor wells (1 through 4), the contact between bedrock and alluvium, and the profile of the bottom of the PRB are also shown. The PRB is not shown in this figure, but it extends to an elevation of 6882 feet, as depicted in Appendix A, Sheet C2, profile A. The elevation of alluvial groundwater in the monitoring wells for mid-May through mid-September is also plotted. Note dry alluvial wells in May, August, and September. Groundwater levels lying below the alluvium-bedrock contact are interpreted as residual groundwater in the well bottoms. A detailed view near and in the PRB is presented in the next figure.

upgradient well became dry in September. Monitor well MCO-4B became dry in August and MCO-5 became dry in September. Although groundwater levels were measured in all of these wells in August and September, the water lies below the alluvium-bedrock contact and is interpreted as residual groundwater in well sumps. As of September 2003, groundwater within the PRB also lies below the alluvium-bedrock contact (Figure 5.1-2). This groundwater is also interpreted as residual water in the bottom of the PRB.

The PRB was designed to accommodate average groundwater flow through the alluvium, with allowance made for high flow conditions. Average groundwater flow was observed in late spring and early summer 2001, a year of average precipitation on the Pajarito Plateau. Under these conditions, saturated alluvium was approximately 10 feet thick. This year, with drought conditions prevailing, the saturated alluvial thickness is far less than normal. Performance of the PRB has been impacted because a small, even

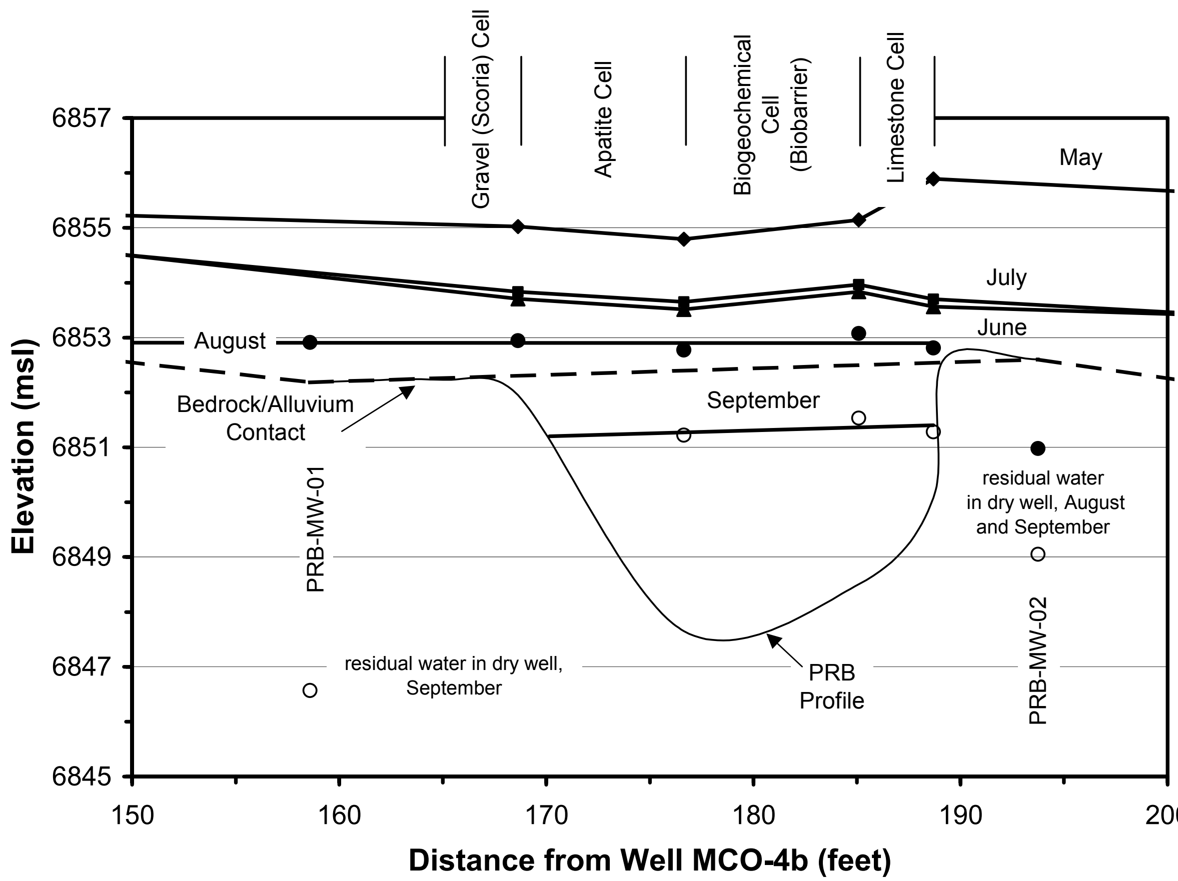

Figure 5.1-2 Hydrogeologic cross-section from west to east through the PRB and PRB monitor wells 1 and 2 in Mortandad Canyon. The contact between bedrock and alluvium and the bottom of the PRB are also shown. Only the lowermost portion of the PRB is depicted, as elements extend to ground surface at an elevation of 6882 feet (Appendix A). The positions of individual cells within the PRB are shown schematically. The elevation of groundwater in the alluvial aquifer for mid-May through mid-September is plotted. Groundwater levels lying below the alluvium-bedrock contact are interpreted as residual groundwater in well bottoms.

negligible quantity of groundwater flowed through it this spring and summer (Figure 5.1-2). As of September, the alluvium near the PRB is dry and groundwater flows have halted.

5.2 Aqueous Geochemistry

This section presents a summary of analytical results from sampling of groundwater in the PRB from May through August 2003. Analytical methods and results and a detailed discussion of data collected during field and laboratory investigations are provided in Appendix C (Table C-1). Temperature, pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), turbidity, total iron, ferrous iron, sulfide, and specific conductance were measured and recorded onsite from an aliquot collected during field sampling. These parameters were measured at the time of sample collection when groundwater was in contact with the atmosphere. Groundwater samples analyzed for inorganic and organic constituents and strontium-90 were collected using dedicated bailers. Both filtered and non-filtered samples were collected for chemical and radiochemical analyses. No analyses of isotopic plutonium or americium were performed because these analyses require large amounts of sample whereas a minimal amount of sample water was available. Consequently, the efficacy of plutonium and americium colloid removal in the PRB was not evaluated.

During the three sampling rounds, pH ranged from 5.83 to 7.11 within the four cells of the PRB. Acidic pH values measured in the phosphate rock (apatite) cell were most likely the result of organic acids (acetate and formate) (Appendix C, Table C-1) produced from the microbial oxidation of solid organic matter. An increase in pH was observed within the bio-barrier and limestone cells. This observation is consistent with dissimilatory nitrate and perchlorate reduction in the bio-barrier cell due to consumption of hydrogen ions during the reactions. The near-neutral pH observed in the limestone cell suggests this cell is performing its function as a final pH control.

Oxidation-reduction potential was measured in the field along with other parameters during sample collection. The groundwater samples were in contact with the atmosphere during the ORP measurements and consequently, the readings were positively biased, which suggest overall oxidizing conditions. Reducing conditions, however, occur within the phosphate rock and bio-barrier cells based on the presence of dissolved organic carbon (DOC) in the form of acetate, formate, and other organic acids and compounds. Concentrations of DO ranged from 1.4 to 7.4 mg/L within the PRB. The lower DO values indicate increasing reducing conditions. The lowest DO measurements were recorded within the phosphate rock (apatite) and bio-barrier cells.

Oxidation-reduction reactions are an important process occurring within the PRB. Variation in concentrations of DOC, carbonate alkalinity, iron, manganese, nitrogen (ammonium and nitrate), sulfur (sulfate and sulfide), chlorine (perchlorate and chloride) and other trace elements within the different cells is evident based on analytical results provided in Table C-1. As groundwater reacts with the different cell material, especially within the phosphate rock and bio-barrier, dissolved oxygen is initially reduced to water, which is then followed by a series of reduction reactions involving nitrate, manganese dioxide, ferric (oxy)hydroxide, sulfate, bicarbonate, and water. A reduction sequence at pH 7 for different solutes and solid phases, with the oxidation state of the element undergoing reduction in parenthesis, is provided below (Longmire, 2002; Langmuir, 1997):

$Cl[VII]O_4^-/Cl[-I]^- \rightarrow O_2[0]/H_2O[-II] \rightarrow N[V]O_3^-/N_2[0] \rightarrow Mn[IV]O_2/Mn^{2+} \rightarrow$

$N[V]O_3^-/N[III]O_2^- \rightarrow N[III]O_2^-/N[-III]H_4^+ \rightarrow Fe[III](OH)_3/Fe^{2+} \rightarrow S[VI]O_4^{2-}/FeS_2[-I] \rightarrow$

$S^0/H_2S[-II]^0 \rightarrow S[VI]O_4^{2-}/\ H_2S[-II]^0 \rightarrow HC[IV]O_3^-/C[-IV]H_4^0 \rightarrow H_2O[-II]\ /H_2(g).$

Perchlorate (ClO_4^-) is a significant contaminant found in Mortandad Canyon. Perchlorate is the dissociation anion of perchloric acid used in actinide research and processing chemistry at LANL. The bio-barrier cell was constructed for enhancing degradation (reduction) of this chemical through microbial processes. During construction of the PRB in February 2003, the concentration of perchlorate in alluvial groundwater was 0.035 ppm. Measurable concentrations of perchlorate within alluvial wells MCO-4B and MCO-5 and the gravel and limestone cells ranged from 0.0015 to 0.017 ppm between May and August. In contrast, concentrations of perchlorate were less than detection (0.002 ppm) within the phosphate rock and bio-barrier cells, an indication that the PRB is destroying perchlorate. The microbial enzyme pathway reduces perchlorate to chlorate (ClO_3^-), then chlorite (ClO_2^-). Chlorite is then enzymatically dismuted to chloride and water. Solutes produced from the reduction of perchlorate, including chlorate and chlorite, were measured between May and August, a further indication that the PRB is destroying perchlorate.

Activities of strontium-90 measured in May and July ranged from 18 pCi/L within the PRB to 95 pCi/L in wells outside the PRB (Appendix C, Table C-1) Strontium-90 data for samples collected in August were not yet complete at the time this report was written. The lowest activity of strontium-90, measured in the central port of the phosphate rock cell, represents a 79 to 81 percent decrease in activity of this radionuclide relative to the pre-existing activity in groundwater. It is hypothesized that strontium-90 adsorbed onto the phosphate rock to produce this decrease in activity. The reduced activity observed for strontium-90 suggests the PRB is immobilizing this radionuclide to levels below the DOE derived concentration guideline. Slightly higher activities of strontium-90 occur in groundwater within the north and south perimeters of the two cells. The non-uniform distribution of strontium-90 may result from varying residence time and saturated thickness of pore water within the phosphate rock cell. Up to 41 percent removal of strontium-90 from groundwater was observed within the bio-barrier cell. Partial adsorption or cation exchange of strontium-90 onto solid organic matter within the bio-barrier cell is possible based on differences in observed activities of this radionuclide measured within the bio-barrier and the gravel and limestone cells. Mitigation of strontium-90 in the bio-barrier, while not specified in the original design, enhances the effectiveness of the PRB.

Concentrations of dissolved iron, manganese, and molybdenum varied considerably during the three sampling events because of extreme gradients in redox potential established within the PRB (Appendix C, Table C-1). Measurable concentrations of dissolved iron and manganese ranged from 0.03 to 7.79 ppm and from 0.002 to 1.06 ppm, respectively. Reductive dissolution of ferric(oxy)hydroxide and manganese oxide-hydroxide present as trace phases within the phosphate rock and bio-barrier cells may account for elevated concentrations of iron and manganese. Microbial reduction of both iron and manganese may also be occurring.

Measurable concentrations of dissolved molybdenum ranged from 0.002 to 0.075 ppm with the lowest concentrations occurring within the phosphate rock cell and the highest concentrations occurring within the gravel and limestone cells (Appendix C, Table C-1). Detectable concentrations of dissolved arsenic ranged from 0.0004 to 0.0044 ppm with the highest concentration occurring in the phosphate rock. Concentrations of arsenic are below the current maximum contaminant level (MCL) of 0.050 mg/L. Natural arsenic is a trace element associated with the phosphate rock in which 0.006 ppm (by weight on the dried solid) was leached using deionized water (Appendix C, Table C-2). Detectable concentrations of dissolved uranium ranged from 0.0001 to 0.0032 ppm with the highest concentration occurring in the limestone. Concentrations of uranium upgradient, within, and downgradient of the multiple PRB are below the MCL of 0.030 mg/L. Natural uranium is a trace element associated with the phosphate rock in which 0.025 ppm (by weight on the dried solid) was leached using deionized water (Appendix C, Table C-2).

The highest concentrations of ammonium (6.97 to 16.0 mg/L) were measured in the phosphate rock and bio-barrier cells and most likely resulted from reduction of nitrate through a microbial process known as nitrate ammonification. Concentrations of ammonium upgradient (MCO-4B) and downgradient (MCO-5) of the multiple PRB are less than 0.1 ppm (Appendix C, Table C-1), suggesting that oxidizing conditions prevail with respect to nitrogen species. Concentrations of nitrate were less than detection (0.01 ppm) within the phosphate rock and bio-barrier cells during the second and third sampling rounds. Concentrations of nitrate (as nitrate), however, ranged from 7.86 to 12.2 ppm within the gravel and limestone cells. Concentrations of sulfate measured in monitoring wells MCO-4B and -5 and in the gravel and limestone cells ranged from 45.9 to 53.4 ppm. Concentrations of this solute commonly were less than detection (0.02 ppm) within the phosphate rock and bio-barrier cells during the three sampling rounds (Appendix C, Table C-1). Non-detectable concentrations of sulfate suggest that sulfate reduction has taken place within the phosphate rock and bio-barrier cells by the action of sulfate-reducing bacteria.

Since concentrations of perchlorate, chlorate, and chlorite in the limestone cell are similar to upgradient well concentrations rather than diminished concentrations observed within the phosphate rock and bio-barrier cells, groundwater flow through the PRB is taking place at a very slow rate. Varying distributions of ammonium, nitrate, sulfate, iron, and manganese within the phosphate rock, bio-barrier, and limestone cells also support this hypothesis. The geochemistry of the PRB is consistent with the hydrogeologic interpretation of impacted performance due to negligible quantities of groundwater flow.

5.3 Microbiology

As part of the PRB investigation, analysis of groundwater was performed to characterize various microbial and biochemical processes. Selected samples were analyzed for a series of parameters during the first and third sampling events (late May and August 2003). The parameters measured included enumeration studies using Most Probable Number (MPN) analyses for nitrate-reducers and perchlorate-reducers. Additional analyses were performed for perchlorate, nitrate, organic volatile fatty acids (VFA), total and ferrous iron, and other anions. Details of the analytical and microbial characterization results are provided in Appendix D.

The analytical results are presented in Appendix D (Tables D-1 through D-6) for each of the above analytical methods. Samples were analyzed from both late May and August 2003 sampling events, however only the May results are currently available. Groundwater samples were collected for microbial characterization from the following wells and ports install upgradient, within, and downgradient of the multiple PRB:

1) Downgradient well, MCO-5,
2) Upgradient well, MCO-4B,
3) Center port in bio-barrier cell,
4) Center port in phosphate rock (apatite) cell,
5) Center port in gravel cell, and
6) Perimeter port in bio-barrier (north of center).

The results of the microbial investigation (Appendix D) show that active degradation of both nitrate and perchlorate is occurring in both the phosphate rock (apatite) and bio-barrier cells. Total organic carbon analysis of the phosphate rock showed a relatively high amount of carbon present (0.77%), sufficient to account for the levels of degradation occurring in these samples. It is expected that this organic carbon will serve as a carbon source for growth and will be rapidly consumed by indigenous bacteria. In addition to low levels of both nitrate and perchlorate in the groundwater samples collected from the phosphate rock and bio-barrier cells, other evidence for active microbial reduction and growth includes lowered pH and ORP (Appendix C, Table C-1).

Production of metabolic organic acids, utilization of the available oxygen, and production of acetate and propionate as by-products of metabolism (Appendix D, Table D-1) is evident from analyses of the groundwater samples. In addition, the lowered dissolved oxygen (see Appendix C, Table C-1) increased ferrous iron, and decreased ferric iron (Appendix D, Table D-2; Appendix C, Table C-1) provide indications that anaerobic conditions necessary for nitrate and perchlorate reduction are present. Analyses of the north perimeter well in the bio-barrier cell show similar results to those in the center well, but the activity appears to be much lower in response to decreasing saturated thickness in the alluvium during the time of sampling.

Results of the microbial identification studies conducted under perchlorate-reducing conditions imply that the dominant perchlorate-reducing bacteria in these samples were members of the *Dechloromonas* group and were closely related to the perchlorate-reducer *Dechloromonas aromatica* strain RCB. Results of this investigation conducted under nitrate-reducing conditions imply that nitrate reduction was not being mediated by members of the *Dechloromonas, Dechlorosoma,* or *Dechlorospirillum* groups. The enumeration results show the presence of both nitrate- and perchlorate-reducing bacteria in all of the groundwater samples, with only a slight increase in microbial population in the bio-barrier cell. It is expected that the microbial populations will increase in the future, however, most bacteria only grow well in the subsurface that are attached to solid surfaces. Under these growth conditions, only an analysis of the solid materials in the multiple PRB will be adequate to show meaningful changes in the microbial populations.

6.0 Conclusions

Installation of a multi-layered PRB in Mortandad Canyon demonstrates the viability of *in-situ* treatment of a suite of contaminants consisting of metals, inorganic chemicals, and radionuclides. The PRB also serves to mitigate possible vulnerabilities from downgradient contaminant movement within alluvial and deeper perched groundwater within the canyon. The PRB is the first groundwater remediation project installed at LANL, the first multi-layered design of a reactive barrier to be installed in the DOE complex, and the first reactive barrier to target actinides (excluding uranium), strontium-90, and perchlorate.

From analytical results and characterization information obtained during this project, the following general conclusions are drawn:

1) Geohydrologic conditions that constrain groundwater flow in a known, controlled manner are suitable for emplacement of reactive barrier technology. The canyons dissecting the Pajarito Plateau across LANL are an excellent example of a well-constrained geohydrologic system (alluvium).
2) Sequential layering of reactive media in a PRB promotes *in-situ* treatment of a contaminant suite that display a range of dissimilar geochemical properties requiring diverse reaction processes for immobilization or destruction.

The PRB is functioning excellently in that it is removing both nitrate and perchlorate to levels below the method detection limits (MDL). The MDLs for nitrate and perchlortae, using ion chromatography, are 0.01 and 0.002 ppm, respectively. The MCL for nitrate (as N) is 10 ppm and the proposed groundwater risk level for perchlorate is 0.004 ppm. In addition, results indicate that intermediate degradation products such as nitrite and chlorite are largely being reduced to the final products of reduction (nitrogen gas and chloride, respectively) within the residence time of the pore water in the PRB. The multiple PRB is removing 40 percent (bio-barrier) to 81 percent (phosphate rock) of strontium-90 from groundwater within the central portion of the engineered structure. The PRB is not treating large quantities of groundwater, and is functioning largely in a batch mode, because a small, even negligible quantity of groundwater flowed through it this spring and summer. As of September, the alluvium near the PRB is dry and groundwater flows have halted.

7.0 Recommendations

Measurement of precipitation on the Pajarito Plateau and alluvial groundwater flow in Mortandad Canyon is routinely performed by LANL. These data need to be regularly monitored to determine when groundwater flow returns to Mortandad Canyon. Water levels within monitor wells adjacent to the PRB and ports within the PRB may need to be measured on a quarterly basis if routine surveillance data is ambiguous.

Once alluvial groundwater flow returns to Mortandad Canyon, additional studies and monitoring of both the solid materials and the groundwater will be necessary to thoroughly understand the processes occurring in the multiple PRB, and to predict the rate of utilization and the eventual lifetime of the barrier materials. Specific recommendations include the following:

1) Perform quarterly sampling of monitor wells adjacent to the PRB and ports within the PRB, using a sampling and analytical matrix similar to the one used in this study,
2) Evaluate performance of PRB during conditions of flow relative to current "batch" conditions. In particular, the evaluate the efficacy of plutonium and americium colloid removal, and
3) Sample solids within the phosphate rock cell and the bio-barrier and compare to standards retained in the laboratory.

8.0 Acknowledgements

This document is referenced at Los Alamos National Laboratory as LA-UR number 03-7320. LANL contributors to this project include personnel from the Cerro Grande Fire Rehabilitation Project (Aimee K. Blanchard, Howard Granzow), RRES Division (Roy Bohn, David Janecky, Allyn Pratt, Tom Starke), EES Division (James L. Conca, Don Krier), C Division (Doug Ware, Elmer Garcia, Matt Jones) and SUP Division (Dale Carmichael). Shaw Environmental, Inc. contributor to this project include Elmer Alcon, Wah Tak Chan, Paul Ingersoll, Doug Jerger, Darren Meadows, Kevin Reid, and Zane Tuta.

9.0 References

Bowles, J.E., 1982, Foundation analysis and design: New York, The McGraw-Hill Companies, 1175 p.

Broxton, D., D. Vaniman, P. Longmire, B. Newman, W. Stone, A. Crowder, P. Schuh, R. Lawrence, E. Tow, M. Everett, R. Warren, N. Clayton, D. Counce, E. Kluk, and D. Bergfeld, December 2002. "Characterization Well MCOBT-4.4 and Borehole MCOBT-8.5 Completion Report," Los Alamos National Laboratory Report LA-13993-MS, Los Alamos, New Mexico. (Broxton et al. 2002, 76006)

Coates, J.D. and Achenbach, L.A., 2001, The Biogeochemistry of Aquifer Systems, in Manual of Environmental Microbiology, 2nd Edition, Hurst, C.J., Knudsen, G.R., McInerney, M.J., Stetzenbach, L.D., and Walter, M.W. (Editors), ASM Press, Washington, DC. pp 719-727.

Conca, J., Strietelmeier, E., Lu, N., Ware, S.D., Taylor, T.P., Kaszuba, J., and Wright, J., 2002, Treatability study of reactive materials to remediate ground water contaminated with radionuclides, metals and nitrates in a four-component permeable reactive barrier, *in* Naftz, D.L., Morrison, S.J., Davis, J.A., and Fuller, C.C., eds., Handbook of groundwater remediation using permeable reactive

barriers: Applications to radionuclides, trace metals, and nutrients, Academic Press.
Langmuir, D., 1997, Aqueous Environmental Geochemistry, Prentice-Hall, Inc., Upper Saddle River, New Jersey.
LANL, 2002, Environmental Surveillance at Los Alamos during 2000: Los Alamos, New Mexico, Environmental Surveillance Program, LANL.
Longmire, P., 2002. Characterization Well R-15 Geochemistry Report, Los Alamos National Laboratory Report LA-13896-MS, Los Alamos, New Mexico.
Lovley, D.R. and Phillips, E.J.P., 1987, Rapid assay for microbially-reducible ferric iron in aquatic sediments, Appl. Environ. Microbiol. 53:1536-1540.
Marty, R., Bennett, D., and Thullen, P., 1997, Mechanism of plutonium transport in a shallow aquifer in Mortandad canyon, Los Alamos National Laboratory, New Mexico: Environmental Science & Technology, v. 31, p. 2020-2027.
McDonald, M.G., and Harbaugh, A.W., 1988, A modular three-dimensional finite-difference ground-water flow model, Techniques of water-resources investigations of the Unites States Geological Survey, Volume 6, Chapter A1, United States Geological Survey, p. 576.
PileBuck, I., 2001, Spw 911, V.2.00, Computer Program for Structural Design of Sheet Piling.
Purtymun, W., Buchholz, J., and Hakonson, T., 1977, Chemical quality of effluents and their influence on water-quality in a shallow aquifer: Journal of Environmental Quality, v. 6, p. 29-32.
Purtymun, W., Hansen, W., and Peters, R., 1983, Radiochemical quality of water in the shallow aquifer in Mortandad Canyon, 1967-1978, Los Alamos National Laboratory, p. 18.
Purtymun, W.D., 1995, Geologic and hydrologic records of observation wells, test holes, test wells, supply wells, springs, and surface water stations in the Los Alamos area: Los Alamos, Los Alamos National Laboratory, p. 339.
Shaw Corporation, 2001, Field Summary Report, Phase I, Geotechnical and Hydrogeological Activities for the Multiple Permeable Reactive Barrier, Los Alamos National Laboratory, Mortandad Canyon, Los Alamos, New Mexico: Los Alamos, Los Alamos National Laboratory, p. 18.
Shaw Environmental, I., 2001, Conceptual design report: Multiple permeable reactive barrier (PRB), Mortandad Canyon, Los Alamos, New Mexico: Los Alamos, Los Alamos National Laboratory.
Shaw Environmental, I., 2002, Final design report: Multiple permeable reactive barrier (PRB), Mortandad Canyon, Los Alamos, New Mexico: Los Alamos, Los Alamos National Laboratory.
Wolery, T.J., 1992, EQ3NR, a computer program for geochemical aqueous speciation-solubility calculations: Theoretical manual, user's guide, and related documentation (Version 7.0): Livermore, CA, Lawrence Livermore National Laboratory.